

Processing Characteristic and Liquid Crystalline Phase Behavior of PHB/PEN/PET Ternary Blend

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INTRODUCTION

Poly(ethylene 2,6-naphthalate) (PEN) has been known since 1948, when its synthesis was first reported by ICI. Co.¹ In spite of its long history, application of PEN is limited as compared with poly(ethylene terephthalate) (PET), because PEN monomer is very expensive, and PEN exhibits relatively high melt viscosity that is not easy for fiber spinning and injection molding.² However, PEN is a high performance polyester that exhibits superior physical and chemical properties to those of PET. There is reason in that naphthalene moiety in PEN provides stiffness to the polymer backbone, leading to the improved thermal resistance, excellent mechanical properties and outstanding gas barrier characteristics.³⁻⁶ In recent years, interest in TLC copolyesters has been grown.⁷ Binary copolyesters of poly(*p*-hydroxybenzoic acid) (PHB)/PET or PHB/PEN and ternary copolyester of PHB/PEN/PET that form TLCP melts have been synthesized, and studied by many researchers.⁸⁻¹¹ Crystallization behaviors and thermal transition temperature including LC phase transition temperature have been reported. These investigations reveal the followings:

- (1) Ternary copolyesters containing 30 mol% PHB are partially LC phase, and those containing over 50 mol% PHB are completely LC phase.⁸
- (2) In the copolyesters containing up to 50 mol% PHB, both PET and PEN crystals are formed. In those containing 80~90 mol% PHB, only crystals of PHB are observed.⁹
- (3) Ternary copolyester of PHB/PEN/PET (30/35/35) is in LC phase up to 160°C, where it starts to become gradually isotropic, and it is completely isotropic at 290°C.¹⁰
- (4) For PET/PEN copolymers no LC phase is formed.⁸

In this research, commercially available PHB/PET copolyester LCP, PEN and PET are mechanically blended to pursue LC phase of blended articles. The critical composition of PHB in the PEN and PET to show LC ternary blended articles are investigated, and miscibility and thermal behavior are studied by thermal analysis. In addition, the relationship between mechanical property and morphology of ternary blends with different PHB contents are observed by SEM micrograph of tensile bar after tensile testing.

EXPERIMENTAL

TLCP used in this research was a TLC copolyester, Rodrun 5000 (Unitika Co., Japan), supposed to be prepared from 80 mol% PHB and 20 mol% PET; hereafter poly(HB/ET) (8/2) LCP. The PEN with an intrinsic viscosity of 0.51 dL/g was supplied by courtesy of Kolon Co. in Korea. The PET with an intrinsic viscosity of 0.64 dL/g was prepared by courtesy of Samyang Co. in Korea. The blends were made by melt blending in a Haake Rheomix 600 at 285 °C for 5 min with different compositions. Thermal behavior of blends was conducted in Perkin-Elmer DSC-7. Tensile testing specimens were prepared using Minimax Molder model CS-183 MMX (CSI Co.) at 290 °C. Tensile tests were performed using UTM 10E (United Calibration Co.) according to ASTM-D638 method. Morphology of fracture surface for the narrow section of tensile bar prepared by injection molding were observed at perpendicular to the injection flow direction using a SX-30E SEM (Topcom Co.).

RESULT AND DISCUSSION

Thermal behavior

DSC measurements of PEN/PET blends on several compositions prepared by melt blending are shown in Figures 1. In the dependence of melting behaviors on the composition, melting temperature (T_m) and melting enthalpy (ΔH_m) appear its lowest value at a PEN/PET (50/50) composition. It indicates that at this composition the achievable crystallinity is the smallest or the crystalline structure formation is the least perfect. DSC thermograms of PHB/PEN/PET blends are shown in Figure 2. All blends have one T_g , and T_g of blends is slightly increased with increasing PHB content. Moreover, melting temperature of blends are increased with increasing PHB content.

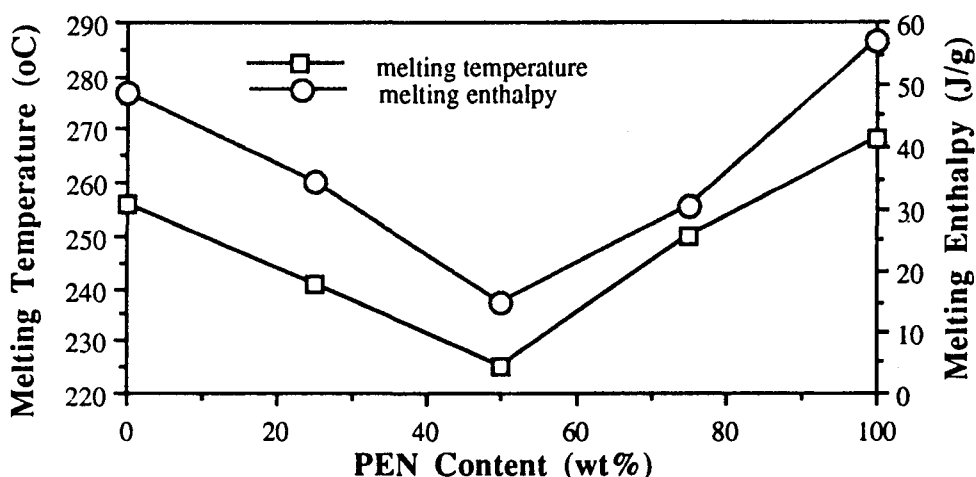


Figure 1 Melting temperature and melting enthalpy as a function of PEN content for the PEN/PET blends.

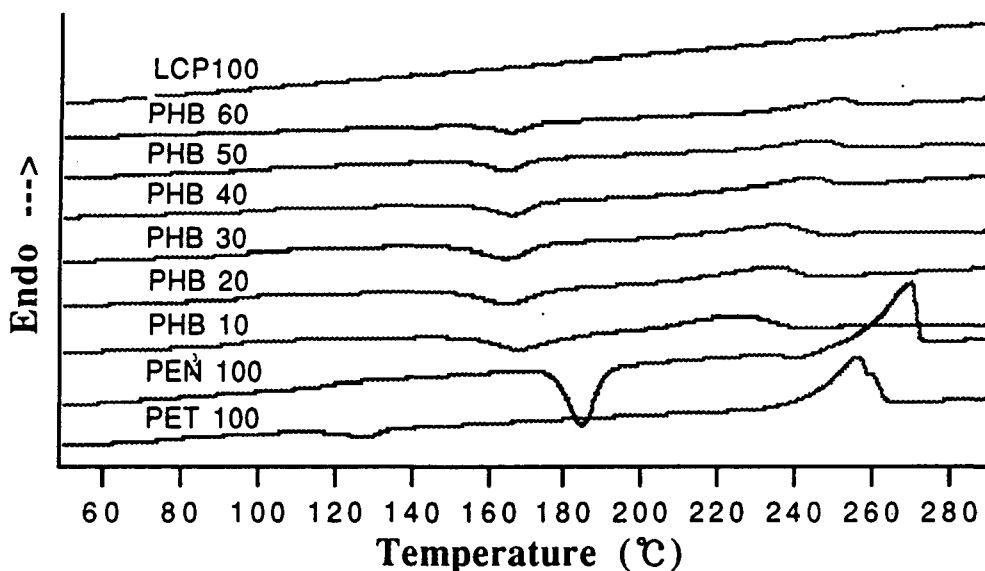


Figure 2 DSC scans of PHB/PEN/PET blends which were heated to 280°C at the rate of 200°C/min, and held for 2 min then cooled to 0°C (heating rate of 10°C/min).

Mechanical properties

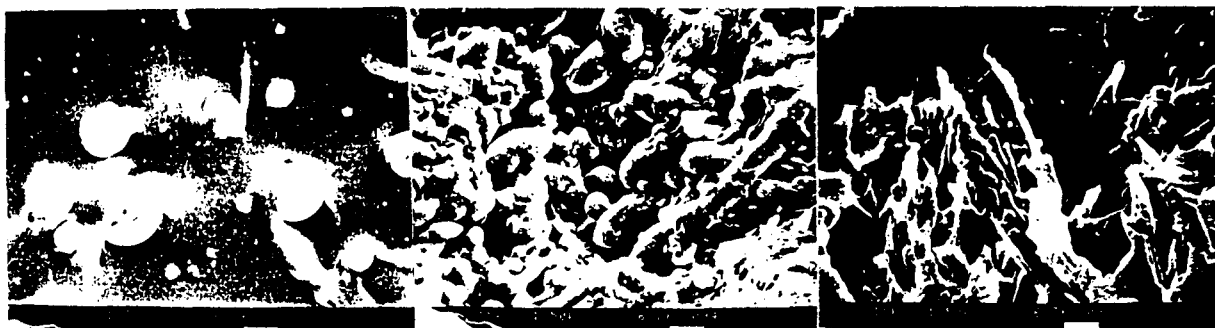
The dependence of mechanical properties of PHB/PEN/PET blends on PHB content are estimated by tensile. Mechanical properties of blends are greatly affected by the PHB content, as shown in Table 1. At the blends of 10 and 20 wt% PHB, tensile strength and initial modulus are relatively low compared to pure PET and PEN, because spherical LCP domains irregularly disperse in PEN and PET matrix polymer. However, tensile strength and initial modulus of blends containing above 30 wt% PHB are improved with increasing PHB content due to the formation of fibrils and LC rich phase in the blend. Therefore, the major factor in increasing mechanical properties of blends is the formation of LCP fibrillar structure depending on processing condition and blending composition.

Table 1 Tensile strength and modulus of PHB/PEN/PET blends which were molded at 290 °C.

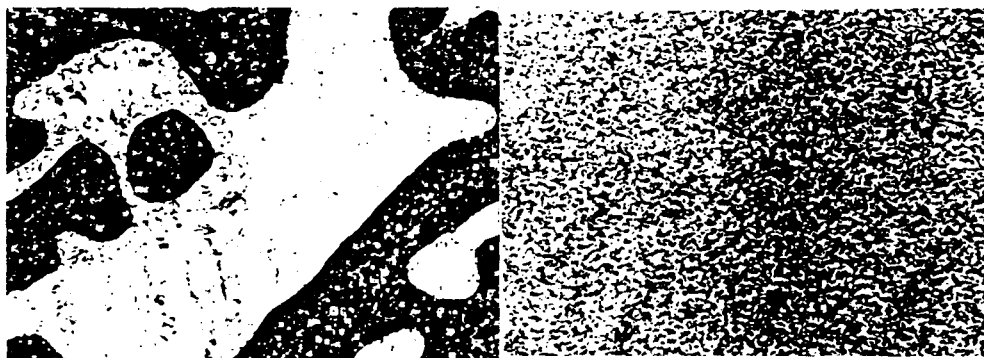
PHB/PEN/PET (wt%)	Tensile strength (MPa)	Modulus (GPa)
0/0/100	23.9	0.68
0/100/0	21.1	0.79
10/45/45	16.8	0.35
20/40/40	13.7	0.20
30/35/35	26.9	2.11
40/30/30	30.8	2.41
50/25/25	54.7	2.82
60/20/20	68.6	3.10
70/15/15	75.9	3.19
80/0/20	90.3	3.21

Morphology

SEM micrographs of narrow section of tensile bar after tensile testing are represented in Figure 3. SEM taking location of tensile bar is perpendicular to flow direction at near skin portion. In the blends of 20 wt% PHB [Figure 3 (a)], the micrographs of perpendicular to flow direction clearly show the formation of circular LCP domains, and these form irregularly dispersed spherical domains with a diameter of $0.4 \sim 12.6 \mu\text{m}$ in the matrix polymers. The micrographs of 30 and 40 wt% PHB [Figure 3 (b, c)] show the LCP ellipsoidal domains and fibrils, and the fibrils are increased with increasing PHB content. It is expected that the mechanical property of blends is improved by the LCP fibrils. Therefore, the effect of PHB content on the morphology of blends is found that the fibrils form above 30 wt% PHB content. However, spherical LCP domains irregularly disperse in the PEN and PET phase below 20 wt% PHB content. Polarized optical photographs of blends are shown in Figure 4. The results observed from 30 wt% PHB reveal that partially LC phase shows in the blended polymers. However, the blend of 40 wt% PHB shows *pseudo* LC phase. It is similar result that the synthesized copolyesters by Zachmann *et al.*⁸ containing 30~40 mol% PHB form LC phase.



(a) PHB/PEN/PET (20/40/40), (b) PHB/PEN/PET (30/35/35), (c) PHB/PEN/PET (40/30/30)
Figure 3 SEM micrographs of PHB/PEN/PET blends molded at 290 °C in Minimax molder; narrow section of tensile bar.



(a) PHB/PEN/PET (30/35/35) (b) PHB/PEN/PET (40/30/30)
Figure 4 Polarized optical photographs of PHB/PEN/PET blends; x400

CONCLUSIONS

The thermal behavior, mechanical properties and morphology of PHB/PEN/PET blends have been studied as a function of PHB content. According to the thermal analysis, melting temperature and enthalpy of PEN/PET blends appeared its lowest value at a 50/50 composition. It indicated that crystalline was the smallest or the crystalline structure formation was imperfect. For the PHB/PEN/PET blends, glass transition temperature and melting temperature were increased with increasing PHB content. In tensile testing, tensile strength and initial modulus of the blends were low at 10 and 20 wt% PHB. However, the blends containing above 30 wt% PHB were improved with increasing PHB content due to the formation of fibrous structure. According to the morphology, the blend of 20 wt% PHB was formed irregularly dispersed spherical domains with a diameter of 0.4~12.6 μm in the matrix polymers, and the blends of 30~40 wt% PHB were observed LCP ellipsoidal domains and fibrils. Fibrils were increased with increasing PHB content. It was expected that the mechanical properties of blends were improved by the LCP fibrils. In addition, the polarized optical photographs of blends were observed partially LC phase at 30 wt%, and the blend of 40 wt% PHB was shown *pseudo LC* phase.

Therefore, the critical composition of PHB in the matrix polymers to show *pseudo LC* phase was 40 wt%, and fibril formation to improve mechanical properties was observed above 30 wt% PHB.

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